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Membrane Filtration of Colloidal Silica

A cost-effective and efficient solution

Study

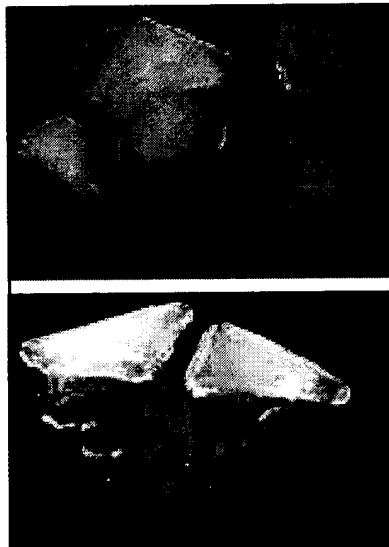
Background

New Logic Research's patented V◇SEP membrane filtration system has been installed at Silica Gel processing plants. Vibrational membrane filtration is an innovative new way to dewater or diafilter Silica product. V◇SEP can be used as a pre-treatment for a spray dryer or evaporator. It can replace other less reliable pre-treatment systems such as Centrifuges. Today's Industrial Silica market is very competitive and efficiency in operating costs can make the difference. The V◇SEP system consumes about 12 kW of electricity and can reduce the gas consumption of a spray dryer by an average of 700,000 Therms/year. Also, the power consumption of a V◇SEP system is 10-20 times lower than Centrifuges.

New Logic's vibrating Membrane System is currently being used for dewatering of PVC Latex, Paper Coatings, Titanium Dioxide, Latex Paint Wastewater, and many other thick slurries where volume reduction is desired. There are Silica customers who are using V◇SEP to diafilter the slurry to wash it and remove impurities and salts and for product recovery from wastewater during wash down.

Characteristics

Colloidal Silica comes in many forms and has many unique properties. It has a strange and widespread number of uses. It is used as a viscosity additive for the latex in tennis shoe soles and is also used for de-inking during paper recycling. Colloidal Silica has many unique characteristics that make it useful. The man-made amorphous type has no defined shape and the surface of the particles has great molecular charge. Just as the coastline of Norway is saturated with fjords giving a very



small country one of the largest coastlines in the world, the surface area of amorphous Silica is incredibly large in relation to its size. Silica Gel has a surface area equal to 700m²/g. Only activated carbon has a higher surface area. Another way to illustrate this is that the surface area of one teaspoon of colloidal Silica gel is equal to more than one football field in size.

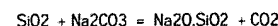
Fumed Silica is more densely gathered due to its chemical synthesis process. Silica Gel is a suspension solution of random colloidal silica without definite form or size. The particles in the solution form a loose network due to the "Brownian Motion Theory" which describes the random collision of fluid molecules against the suspended matter. Because the particles repel each other, they are evenly dispersed and will not settle out. In addition, colloidal silica will have a very high viscosity and a low gel point. Colloidal Silicas and other Silicates can have Gel points as low as 15-35%. The gel point is the concentration at which the fluid will not flow and cannot be pumped.

Raw Materials

The main ingredient for amorphous silica is regular quartz sand which can be found in abundance anywhere. This sand is processed with Sodium Carbonate, Na₂CO₃ which is made using the Solvay process combining salt, ammonia, carbon dioxide, and limestone all naturally occurring substances.

Silica Gel:

Step One, sand is fused with Sodium Carbonate in a high temperature furnace. The result is Sodium Silicate and Carbon Dioxide gas.



Step 2, the Silica Gel is made using Sulfuric Acid:



The result is an aqueous salty solution containing Silica colloids. The Sodium Sulfate salts must be washed using diafiltration and then the Silica must be partially dewatered. The exact methods used will vary, however, most all silica ends up in a salty solution that must be rinsed and then dewatered.

Silica Gel Production Process

During the refining process, the colloidal Silica is suspended in a salty aqueous slurry. This slurry must be desalted and dewatered. V◇SEP is uniquely able to be used as a diafiltration process and then to dewater in a single pass. During diafiltration, a UF membrane is used which will reject the particles and allow the salty water to pass through the membrane. By successive rinses, the silica can be completely separated from the salt solution. The resulting gel is nearly pure colloidal silica with some water.

Colloidal Silica sells for about \$25 per Pound. While in production, 2.3 tons of product is recovered each hour per 84" V◇SEP.

V◇SEP ... A New Standard in Rapid Separation

Silica: Silicon Dioxide, SiO_2 . Occurring naturally as a crystal, as in sand, or manmade using chemical processing to become a colloidal group of particles which have non-defined amorphous shapes.

Silica Gel: The word "Gel" in the name is misleading. Silica Gel is one form of colloidal silica which is produced by reacting Sodium Carbonate with pure Silica Sand with pressure, temperature, and Sulfuric Acid as one step. Silica Gel is a colloidal Silica which is a man-made suspension of solid particles in a liquid which forms a loose network.

Fumed Silica: This is another man-made type of colloidal Silica. It is produced by reacting Silicon Tetrachloride, SiCl_4 , with water and steam. It is more pure and lacks the surface charges of Silica Gel. As a result, its properties and uses are different.

Precipitated Silica: This is another form of colloidal Silica. It is produced by yet another chemical synthesis process giving unique properties.

Silicate: Generic name for any metallic compound also containing Silica, ie $\text{Na}_2\text{O} \cdot \text{SiO}_2$

Silica Zeolite: Alumino-Silicate, $(\text{Al}_2\text{O}_3 \cdot \text{SiO}_2)$ main component of Clay, which is naturally hydrated. The material is dewatered and the interlocked water molecules are also removed by calcination resulting in a molecularly charged receptor for other molecules.

Diatomaceous Earth: Naturally occurring decayed remains of "Diatoms" which are a form of unicellular algae having silica casings for bodies. The decomposed material closely resembles man-made amorphous silica as it is not cubic crystalline shaped like Silicon Dioxide normally is in nature.

Siliceous: Any substance containing Silicon Dioxide, (Silica)

Fine Ground Silica: Created by grinding pure Silicon Dioxide sand to form a powder. Not the same as colloidal silica because the particle still have uniform crystalline shape although very small in size. Because the particles are dense crystals, they lack surface area and don't have the adsorptive qualities of amorphous colloidal silica.

Activated: Similar to Clacined which is driving off liquid ingredients using extreme heat just below the melting point of the material. Activation is driving off gases in the same manner using extreme heat. The remaining product has very good adsorption properties, ie activated carbon.



New Logic's patented V-SEP equipped with 1300 SF (120m²) membrane for the treatment of Chemical Processing dewatering

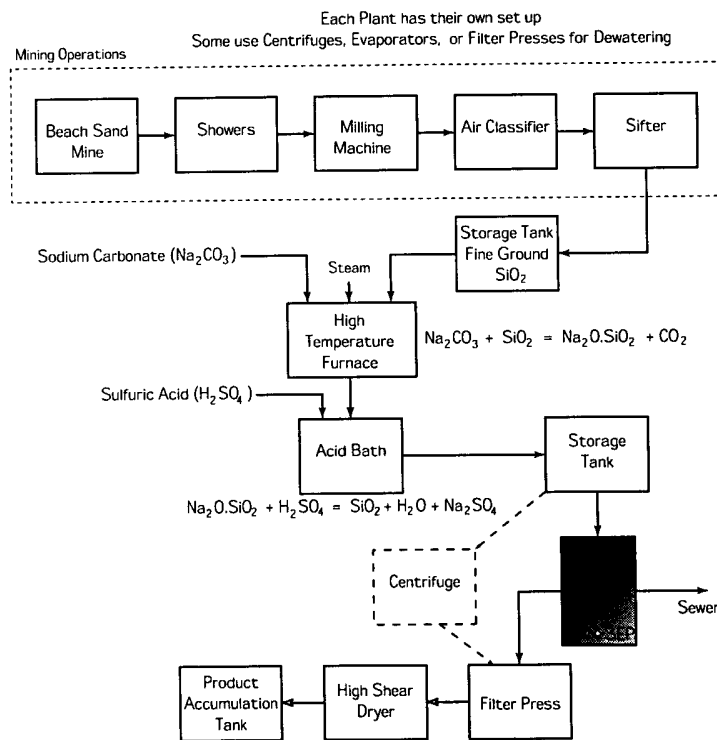
New Logic's Solution

Technological advances in membrane filtration systems and membranes have created an opportunity for the efficient and economical treatment of Silica Diafiltration and Concentration. The "Vibratory Shear Enhanced Process" or V-SEP[™] developed by New Logic makes it possible to filter chemical processing streams without the fouling problems exhibited by conventional membrane systems.

In this case study, the V-SEP membrane system utilizes an Ultrafiltration membrane which will reject the suspended solids and colloids. New Logic uses over 200 membranes and tighter RO and NF membranes are available.

V-SEP is capable of handling thick slurries and concentrating the feed stream to a sludge which can be dried. The filtrate from this can be reused for washdown operations, used as plant water, or sewer. The V-SEP can be used by itself or in conjunction with other equipment for a comprehensive treatment system.

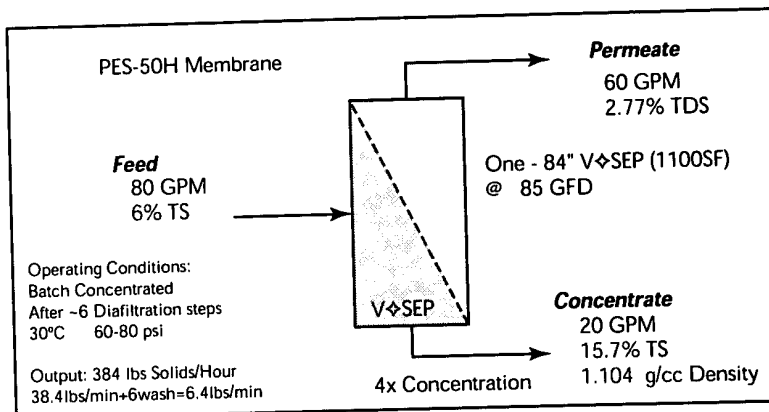
V-SEP ... A New Standard in Rapid Separation



Silica Gel Process Block Diagram

V \diamond SEP is capable of handling influent streams in a single pass with very little pre-treatment. Usually just a 100 mesh prescreen is all that is required. In this case study, the V \diamond SEP was used to replace a centrifuge. The Block diagram below shows the treatment system. The raw process feed enters the feed tank at the left of the drawing. From here it goes to a bag filter and then to the V \diamond SEP machine itself. The concentrate is returned to the feed tank for successive washes until the conductivity reached the design target at which time it is diverted to the concentrate holding tank for further treatment, The Filtrate is partially reused in washdown operations and partially sewered.

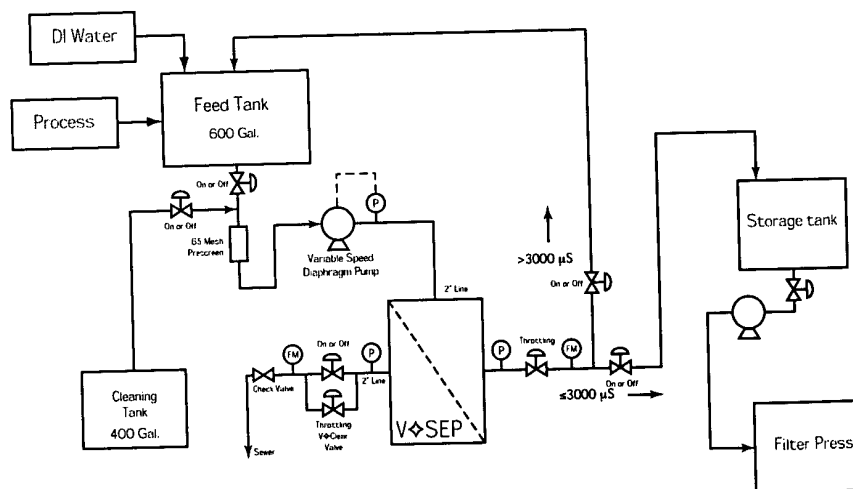
The membrane treatment system can process at a rate of about 80 GPM (18 m³/hr). The process feed containing salts is first concentrated to remove the bulk of the water. Then, with a process of wash volumes, water is added and the removed thus diluting and removing the unwanted salts and other dissolved



contaminants. The operating conditions are 30°C at about 80 psi using an Ultra-filtration membrane. The footprint of the VSEP is about 16 SF (1.5 M²).

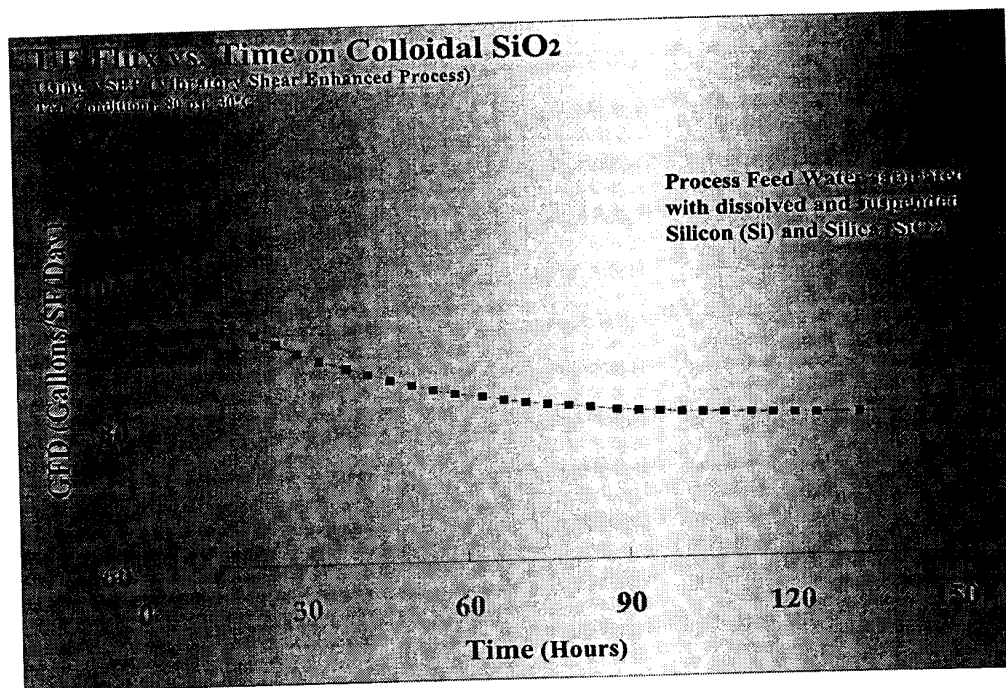
This rate of production would be equal to about 105,000 gallons per day. The concentrate produced is about 15% total solids which is very near the Gel Point with extremely high viscosity. This stream is sent for further processing using other equipment.

A group of small particles suspended in a solution from about 10 nm to 1.0 μm . These particles have non-defined random shape and size and differ from other particles which have uniform shape or size.



System Operation:
This process is run in manual mode and the raw product is diafiltered in the feed tank until enough of the salts and impurities are removed to meet the design criteria of the final Silica product. Diafiltration includes 6 washing steps where an equal volume of De-ionized water is first added to the feed tank. Then the tank is batch concentrated by removing permeate from the system until the volume returns to the original before adding water. Then more water is added to the tank. This process repeats 6 time or until the conductivity of the concentrate is less than 3000 μS . Once the concentrate is within specification, the concentrate from the VSEP unit is diverted to another feed tank where it is stored for use by a filter press or other means of final concentration

V◇SEP ... A New Standard in Rapid Separation



The VSEP is periodically cleaned using a caustic cleaner to reset the flux and produce consistent long term results.

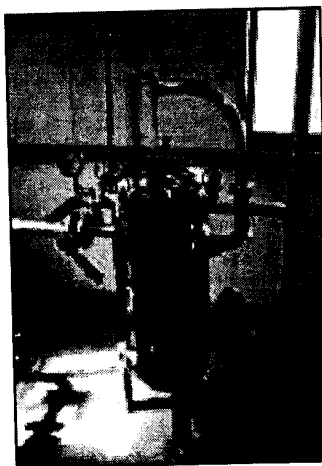
System Throughput

The VSEP system performance is a function of temperature, % recovery, & % Total Solids in the feed slurry. The more concentrated and colder the feed, the lower the throughput of the VSEP system. Temperature affects the viscosity of the liquid and viscosity affects the liquid fraction's ability to move through the membrane surface. In general, one 84" VSEP is capable of producing 60-80 gpm of clean water filtrate from Colloidal Silica at a recovery of 75% of the total volume as permeate.

System Components

The process feed is pulled out of an existing 5000 gal feed tank. The tank is located near to the VSEP and the feed

pump of the VSEP system is able to prime with only head pressure from the tank. The liquid transfers through a pre-screening unit to remove large particles, (100 mesh). There are many types of mechanical screens that could be used. The picture below shows the type used.



The feed water then flows into a vertical multistage centrifugal feed pump

which provides the pressure to the Filtration unit. The bag filters and pumps are provided with the VSEP system and are skid mounted for easy installation.

The VSEP system comes with a cleaning tank and many of the valves and other interface equipment. The system is "Plug and Play". The feed tank, transfer pumps, heat exchangers, and boiler are not normally included, but, can be provided as part of a complete process package. The VSEP system is automated and controlled by a PLC (Programmable Logic Controller). Operator interface is limited to monitoring the system and making periodic adjustment to parameter settings. The system comes standard with "Foxboro" brand instrumentation including pressure sensors, tank level sensors, flow transmitters, pH analyzers, temperature meters, and conductivity sensors to monitor the process conditions and will send a 4-20 mA digital signal to the PLC for seamless operation.

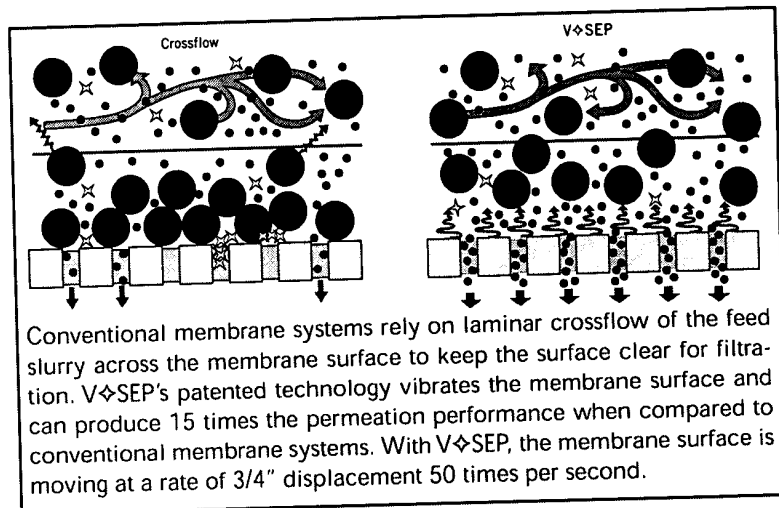
VSEP ... A New Standard in Rapid Separation

Company

New Logic is a privately held company located in Emeryville, California. Incorporated in 1986, New Logic manufactures a proprietary membrane filtration system called V \diamond SEP \circledR (for Vibratory Shear Enhanced Processing). Originally developed for blood plasma separation, the technology has been scaled up to meet the growing separation needs for many industries. V \diamond SEP can be employed in water treatment, product separation, solids dewatering or wastewater treatment. The industries and applications for V \diamond SEP are quite diversified and include: **Pulp & Paper** (black liquor, whitewater, box plant effluent, end of pipe), **Industrial Water Pretreatment** (ultrapure, boiler feed, surface water), **Pigments & Paint** (latex emulsions, product recovery), **Mining** (mine tailings), **Solids Dewatering** (calcium carbonate, kaolin clay, TiO₂), and **Metal Working** (oily wastewater, metal hydroxides).

Technical Services

New Logic has years of experience and expertise in membrane filtration. Their 40,000 sq. ft. facility provides comprehensive manufacturing and facilities. Highly trained engineers and technical staff are available to support your application questions. Feasibility testing can be accomplished in-house, or a fleet



of pilot units are available to support on-site testing. Operational surveys are available to help assess your needs and the potential cost savings. An experienced team of technicians are available to support both on-site pilot work and V \diamond SEP system installations.

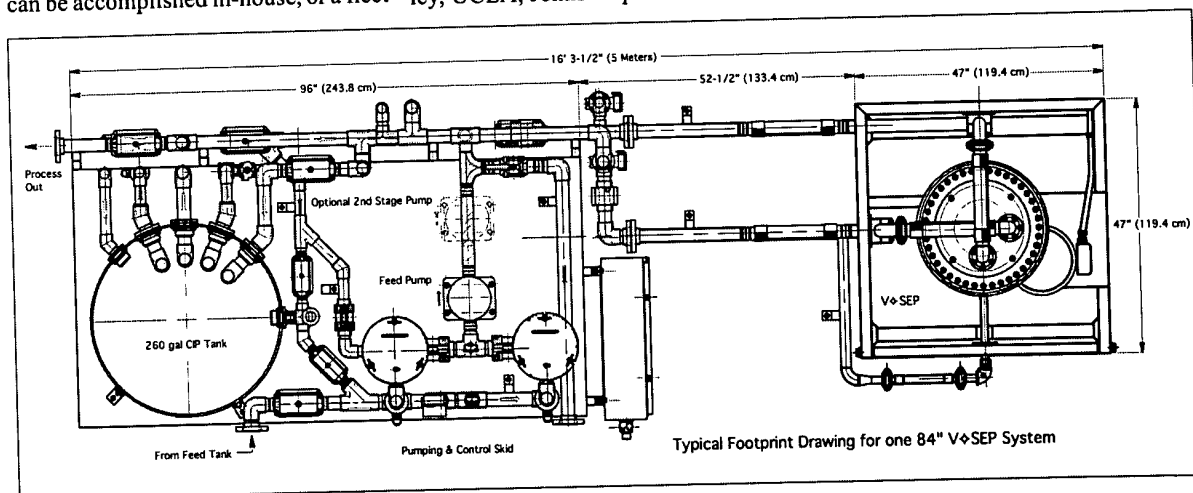
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People

From scientists to customer service associates, New Logic recruits some of the best people available. Academic credentials include doctorates and advanced degrees from such notable universities as Northwestern, Cal Berkeley, UCLA, Johns Hopkins and others.



V \diamond SEP ... A New Standard in Rapid Separation



Fumed Metal Oxides

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Market Application

Overview: Fumed Metal Oxides

Cabot's Fumed Metal Oxides business is made up of two product families: fumed silica and fumed alumina. Products are available in either free flowing powder form or as aqueous dispersions.

Fumed silica is an extremely small particle with enormous surface area, high purity, and a tendency to form chains in the chemical manufacturing process. Particles are formed by injecting chlorosilanes, such as silicon tetrachloride, into a flame of hydrogen and air. The ensuing reaction produces fumed silica and hydrogen chloride.

Fumed silica has two primary functions. Reinforcement increases the strength of various materials, allowing them to be used in a wider number of applications in accordance with the user's exact requirements. Rheology control allows customers to tailor the viscosity of a system to their own requirements.

In some cases, fumed silica can simultaneously enhance different properties of a formulation. For example, fumed silica can give a coating the necessary flow and leveling characteristics to ensure a smooth finish upon drying, while acting as an agent to prevent settling of other ingredients in the formulation.

Fumed silica is sold in the following markets:

- Adhesives & Sealants
- Automotive
- Construction
- Coatings
- Electronics
- Pharmaceuticals
- Printing inks
- Rubber silicones
- Toners

Fumed alumina is produced by the hydrolysis of aluminum chloride in a flame of hydrogen and oxygen. It consists of sub-micron three-dimensional aggregates of primary particles. The aluminum oxide within the particles is in a mixture of crystalline phases, the major one is theta alumina. This differentiates the material chemically from other colloidal forms of alumina, which comprise predominantly the gamma crystalline phase.



Cabot F

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| Property tested | Test methods |
|--------------------------------------|--|
| color | ISO 787, Parts I, XII; ISO 5794, Part I |
| average particle size | ASTM C721, D1366, E20, E523, and F660; ISO 787, Part XVIII |
| SiO ₂ content | ASTM C575 and D297; ISO 5794, Part I |
| coarse, insoluble material | ASTM C117 and D185; ISO 787, Parts III, VI, VII, and VIII; ISO 5794, Part I |
| volatile matter (water) | ISO 787, Part II |
| specific surface area | ASTM D1993 and D5604; ISO 5794, Part I; NF T 45-007 |
| bulk density | ASTM D604; ISO 787, Parts X, XI |
| mean projected area of aggregates | ASTM D3894 |
| metal ion and salt content | ASTM C575 and D719; ISO 5794, Part I, Annexes A, B, C, D |
| absorption of oil | ASTM D2414; ISO 787, Part V |
| pH | ASTM D1512; ISO 787, Parts IV, IX |
| porosimetry | ASTM D4284 |
| occupational exposure | ASTM E1156 |

The typical range of properties for commercial colloidal silicas, silica gels, precipitated silicas, and pyrogenic silicas is given in Table 1.

Table 1. Properties of Commercial Amorphous Silica

| Property | Colloidal silica | Silica gels ^a | Precipitated silica | Pyrogenic silica |
|--|---------------------|--------------------------|------------------------|---------------------|
| SiO ₂ , % | 15-50 | 96.5-99.6 | 85-95 | 98.3-99.8 |
| surface area, m ² /g | 50-750 | 200-800 | 25-700 | 35-410 |
| oil absorption, g/g | 0.9-3 | 1.5 | 1.5-3.5 | 0.5-3 |
| pH, aqueous | 3-5, 8-11 | 2.3-7.4 | 5-9 | 3.5-5 |
| weight loss, % | | | | |
| at 105°C | 50-80 | | 4-7 | 0.5-2.5 |
| at 1200°C | 50-90 | 2-17.5 | 10-14 | 1-4 |
| density, g/cm ³ | 2.2-2.3 | 2.22 | 1.9-2.1 | 2.16 |
| bulk density, g/cm ³ | 1.2-1.4 | 0.1-0.9 | 0.03-3 | 0.03-0.12 |
| particle size | | | | |
| ultimate, nm | 4-60 | 1-100 | 5-50 | 5-50 |
| aggregate, nm | | | 100-500 | 100-1000 |
| agglomerate, μm | | 3-25 | 1-50 | 1-3 |
| refractive index, <i>n_D</i> | 1.35-1.45 | 1.35-1.45 | 1.45 | 1.45 |
| Na ₂ O, maximum % | 1 | 1 | 2 | 0.2 |

^aDry.

Commercial Production

Approximately 40% of synthetic amorphous silica production is in Europe, followed by North America at 30%, and Japan at 12%. Although deposits of naturally occurring amorphous silicas are found in all areas of the world, the most

significant commercial exploitation is of diatomaceous earth in industrialized countries (see DIATOMITE). This is because of the high cost of transportation relative to the cost of the material. Worldwide manufacturers of amorphous silica products are listed in Table 2.

Heterogeneous

Dissolution according to equation 1:

Table 2. Principal Manufacturers of Amorphous Silicas

| Producer ^a | Silica product | Manufacturing location | Capacity, t × 10 ³ |
|--|--------------------------------|--|-------------------------------|
| Akzo | precipitated, gel, colloidal | Germany, Netherlands, Thailand | 85 |
| Bayer | colloidal | Germany | 6 |
| Cabot Corp. | fumed | United States, Germany, United Kingdom | 32 |
| C-E Minerals | fused | United States | 25 |
| Chuo Denko, Denki Kagaku Kogyo, NKK, Showa Denko, and Toshiba Ceramics | fused | Japan | 48 |
| Crosfield | precipitated, gel | United Kingdom, United States | 32 |
| DeGussa | precipitated, fumed, colloidal | Belgium, Germany, India, Japan, Spain, United States | 277 |
| DuPont Chemicals | colloidal | United States | 7 |
| Eka Nobel | colloidal | Sweden, United States | 8 |
| General Electric | fumed | United States | 7 |
| J. M. Huber | precipitated | United States, Finland, India | 136 |
| Minco | fused | United States | 21 |
| Nalco Chemical | colloidal | United States, Europe | 10 |
| Nippon Silica | precipitated | Japan | 18 |
| PPG Industries | precipitated | United States, China, Netherlands, Taiwan, Thailand | 210 |
| PQ Corp. | gel, colloidal, precipitated | North America, Latin America | 20 |
| Precision Electro Minerals | fused | United States | 9 |
| Rhône-Poulenc SA | precipitated, gel | France, Korea, India, United States | 87 |
| Shionogi | precipitated | Japan | 10 |
| Solvay | gel | Germany | 5 |
| Tizayuca | precipitated | Mexico | 8 |
| Tokuyama Soda | precipitated, fumed | Japan | 36 |
| Wacker-Chemie | fumed | Germany, United States | 25 |
| W. R. Grace | gel | United States, Germany | 29 |
| others | gel, colloidal, precipitated | | 64 |

^aIncludes joint venture companies.

^bMay not include captive capacity for intermediates.

^cTotal production capacity.

H_4SiO_4 (aq), which as $\text{Si}(\text{OH})_4$ (aq) or $\text{SiO}_2 \cdot n\text{H}_2\text{O}$. The solubility of SiO_2 in water at 150 ppm SiO_2 (1.2 mmol/kg) at pH 9. The solubility of SiO_2 in water increases with particle size, degree of polymerization, and positive radius of curvature. Particles having a radius of curvature less than 3 nm have a solubility that is significantly greater than that of bulk silica. Particles <3 nm in diameter are highly soluble in water. For example, the solubility of SiO_2 (0.8 mmol/kg) at pH 9 (12.5 mmol/kg) at 25°C is increased fivefold between 0–25°C.

Hydrated amorphous silica. The solubility of amorphous silica is slightly less than that of crystalline silica. The rate of dissolution of amorphous silica is faster than that of aluminum or iron silicates. Amorphous silica is used to remove metal ions from water. Amorphous silica is significant in the behavior of hydrofluoric acid. The solubility of amorphous silica is pH dependent. At a pH value of 9, the solubility of amorphous silica is 10⁻⁴ mol/L. At pH 9, the solubility of amorphous silica is 10⁻⁴ mol/L.

H_2SiO_3

HSiO_3^-

Amorphous silica is used in the synthesis of methanol–water emulsions. Natural biogenic silica. The coating can be used to protect silica surface is biodegradable.

Polymerization of silicic acid particles that can be used for the synthesis of monomers to form polymers.

grow in size and flocculating salts, sils (Fig. 10) (27). the solubility of true solution in and there is no polymerization is l ion at pH >2. -Si-O-Si-, and molecular weight : tetramer, hex- continue to react e Fig. 3). Inter- ation of a small le is anhydrous. articles serve as ause of the sol- osited on larger stwald ripening. les or causes gel ng particle sur-

face charges to enhance aggregation of the particles into three-dimensional gels. The rate of aggregation also increases with dissolved silica concentration in solution. As polymerization occurs, the solution still contains dissolved silica at a concentration equivalent to the solubility of amorphous silica (1,27-29).

Silica Sols and Colloidal Silica

Properties. Colloidal silica is a stable aqueous dispersion or sol of discrete amorphous silica particles having diameters of 1 to 100 nm. Silica sols do not gel or settle out of solution for at least several years of storage. Aqueous sols that contain up to 50% silica have been developed (30,31). Particle sizes of approximately 130 nm in diameter are possible (32), but slowly settle out of solution.

In the absence of a suitable solid phase for deposition and in supersaturated solutions of pH values from 7 to 10, monosilicic acid polymerizes to form discrete particles. Electrostatic repulsion of the particles prevents aggregation if the concentration of electrolyte is below ca 0.2 *N*. The particle size that can be attained is dependent on the temperature. Particle size increases significantly with increasing temperature. For example, particles of 4-8 nm in diameter are obtained at 50-100°C, whereas particles of up to 150 nm in diameter are formed at 350°C in an autoclave. However, the size of the particles obtained in an autoclave is limited by the conversion of amorphous silica to quartz at high temperatures. Particle size influences the stability of the sol because particles <7 nm in diameter tend to grow spontaneously in storage, which may affect the sol properties. However, sols can be stabilized by the addition of sufficient alkali (1,33).

The stability of a silica sol depends on several factors (Fig. 11) and can be controlled by the surface properties of the silica (1). The pH value should be above 7 to maintain sufficient negative charge on the silica particle surface to prevent aggregation. This surface charge is neutralized by soluble salts that ionize and reduce the size of the double layer around the silica surface (Fig. 12), allowing aggregation. Therefore, sols are only stable at low salt concentrations. In the low pH value region sols are metastable, and gelling and aggregation are catalyzed by even very small amounts of fluoride ion. In this low pH value region, water-miscible organic solvents, like alcohol, retard gelling. Gelling occurs more rapidly at higher temperatures and is facilitated by a high silica concentration in the sol.

Silica sols can be destabilized by aggregation, gelation, crystallization, or particle growth plus settling. Aggregation occurs by coagulation in which particles collide or by flocculation in which particles become linked by bridges of flocculating agent (see FLOCCULATION AGENTS). Aggregation is prevented at neutral or lower pH values by the presence of an adsorbed layer of inert material, such as a surfactant, on the silica surface, thus preventing the direct contact of silanol groups with one another. Aggregation, as well as particle growth, is minimized by maintaining either a low silica concentration, a low reaction temperature, and/or a pH value of 9-10. Destabilization of a sol by crystallization of silica rarely occurs because this is a slow process at ambient temperatures (1).

Preparation. To produce sols that are stable at relatively high silica concentrations, particles must be grown to a certain size in weakly alkaline aqueous

nm

particles grow in size
flocculating salts (A),

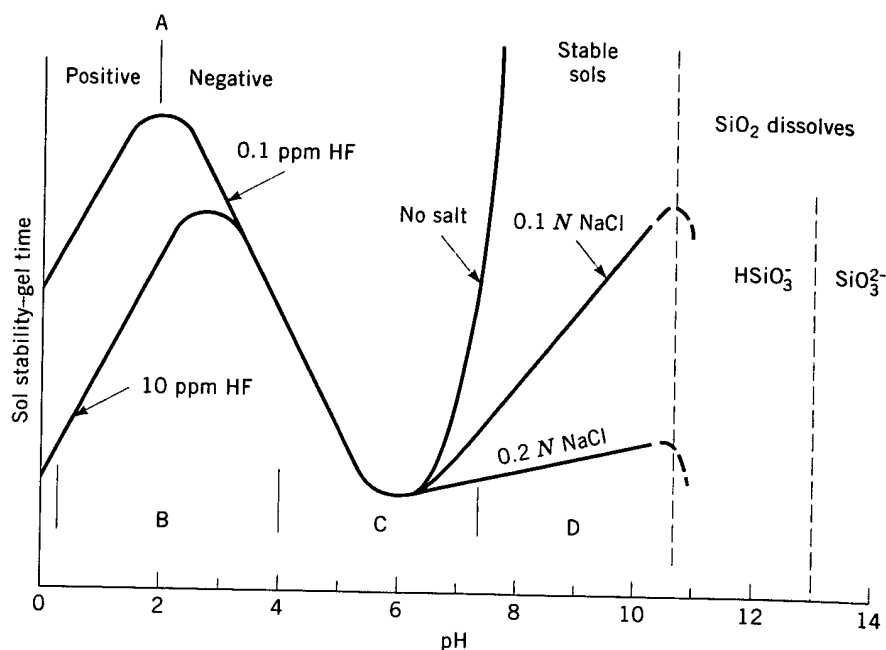


Fig. 11. Effects of pH in the colloidal silica-water system (1), where A represents the point of zero charge; regions B, C, and D correspond to metastable gels, rapid aggregation, and particle growth, respectively. Positive and negative correspond to the charges on the surface of the silica particle.

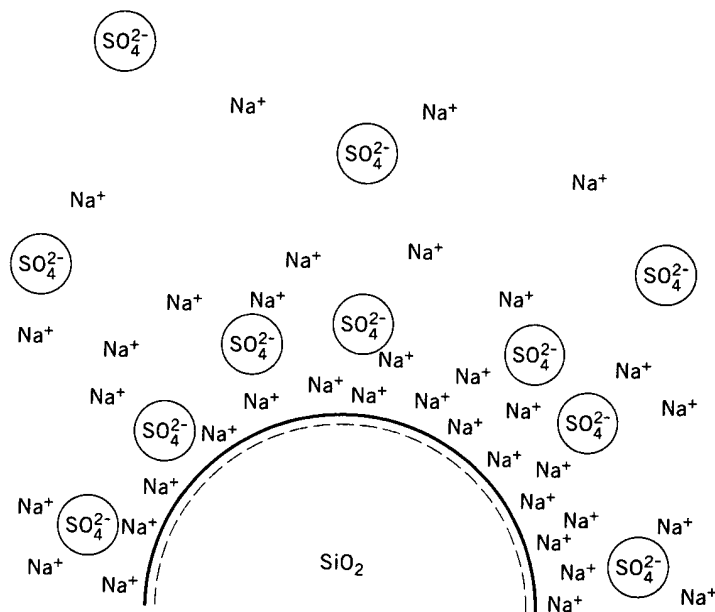


Fig. 12. Salt retention by colloidal particles. The curved dashed and solid lines represent the surface of a negatively charged silica particle. Around this there is a layer of counter sodium cations; outside there is a layer in which sulfate anions (O) are more concentrated than in the bulk solution.

dispersion. Sols of silicate with acid concentration is elevated temperature formation of low ions from the sodium resin to form act stored at 82–100 which can then be the salt from a film and pressure; (4) isopropyl alcohol (5) cleaning pulv coating, which can hydrogen gas and and (6) oxidizing in the presence of are partly coalesced difficult to disperse other dispersing aggregates. A del

Silica sols can be purified by electrodialysis, or ultrafiltration, ultrafiltration, ultrafiltration. A presence of the growth of microprecipitation evaporation is deposited on the evaporation must diameter are concentrated collects near the interface that are low in surface area

Modification subsequent drying values of 4 to 6. It is a function (qv). Further addition of a sol is possible by neutralizing the surface charge to induce coagulation. Additional surface hydroxyl groups by silica surfaces as bridging compounds or polyacrylamide or polyacrylamide

Sol particles are composed of aggregates with a large surface area than

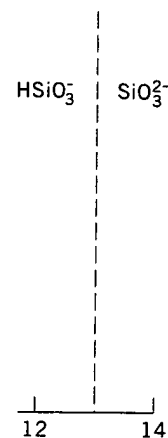
dispersion. Sols can be prepared by (1) neutralizing a dilute solution of sodium silicate with acid to a pH value of 8–9. A sol is produced if the sodium salt concentration is $<ca\ 0.3\ N$ and the neutralization reaction is performed at elevated temperatures to promote rapid particle growth. Rapid mixing prevents formation of low pH regions where gelation might occur; (2) washing sodium ions from the sodium silicate solution by electrodialysis or using an ion-exchange resin to form active silica, ie, low molecular weight polysilicic acid (1), which is stored at 82–100°C. Additional active silica is added to grow the sol particles, which can then be concentrated by evaporation or ultrafiltration; (3) washing out the salt from a freshly formed silica gel and peptizing at elevated temperature and pressure; (4) hydrolyzing $SiCl_4$ or organosilicates, such as ethyl silicate plus isopropyl alcohol. However, such sols are generally not stable and gel quickly; (5) cleaning pulverized silicon metal with hydrofluoric acid to remove the oxide coating, which causes a reaction with water in an alkaline medium to produce hydrogen gas and colloidal silica, which can be stabilized as a sol with alkali; and (6) oxidizing $SiCl_4$ or ethyl silicate at high temperature, or vaporizing silica in the presence of a reducing agent to give pyrogenic silica powder. Particles are partly coalesced, have a low concentration of surface silanol groups, and are difficult to disperse in water to form sols without the addition of a wetting or other dispersing agent, or such treatment as grinding. The resultant sols contain aggregates. A detailed review of silica sol preparation methods is available (1).

Silica sols can be purified with the aid of an ion-exchange resin, dialysis, electrodialysis, or washing. Washing is usually affected by centrifugation, flocculation, ultrafiltration, or electrodecanting, followed by redilution and re-concentration. A preservative such as formaldehyde is sometimes added to prevent the growth of microorganisms. Sols are concentrated by evaporation using forced-circulation evaporators. If the sol becomes too concentrated, a hard layer of silica is deposited on the equipment walls, especially on heat-exchanger surfaces, so evaporation must be carefully monitored. Sols having particle size $>30\ nm$ in diameter are concentrated by centrifugation. Ultrafiltration (qv), where the sol collects near the impermeable filter, can be used to remove water and salts. Sols that are low in soluble salts are concentrated by electrodecantation (1).

Modifications. Coagulation, flocculation, or gelation of silica sols and their subsequent drying produce amorphous silica powders. Gelation is rapid at pH values of 4 to 6. It is effected by increasing the silica content, such as by evaporation (qv). Further drying of the resulting gel yields colloidal aggregates. Coagulation of a sol is prevented by surface charge and surface hydration; conversely, neutralizing the surface charge by lowering the pH value or by adding salt causes coagulation. Addition of salts also causes surface adsorption of cations that reduce surface hydration. Polyvalent cations such as Al^{3+} are strongly adsorbed by silica surfaces and neutralize the surface charge. Hydrated metal cations act as bridging compounds or flocculating agents (qv) for silica particles. Flocculating agents used with silica sols are cationic surfactants (qv) such as octadecyltrimethylammonium bromide or organic polymers such as polyethyleneimine or polyacrylamide (1).

Sol particles are extremely small, and particulate silica obtained from sols is composed of aggregates or porous particles that have a much higher specific surface area than estimated from apparent size. Aggregates are also called

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average pore diameters of 2.2–2.6 nm, and a pore volume of 0.37–0.40 mL/g. This regular density silica gel contains approximately 6 wt % water as surface hydroxyl groups, which imparts a high capacity for adsorption of water and other polar molecules (see DESICCANTS). The gel exhibits a high selectivity for polar molecules and has a large percentage of small pores. Intermediate density silica gel consists of larger ultimate particles having a lower (300–350 m²/g) surface area, larger (0.9–1.1 mL/g) pore volumes, and larger (12–16 nm) average pore diameters. Because of the large pore size, intermediate density silica gel has a high capacity for water adsorption at high humidities. It is often used as a fine powder because aggregate (or secondary) particle size and porosity can be controlled. Low density silica gel (such as an aerogel) has lower (100–200 m²/g) surface areas, larger (18–22 nm) average pore diameters, and larger (1.4–2.0 mL/g) pore volumes. It is usually prepared as a very fine powder of extremely low density. Shrinkage of the gel during drying is minimized.

Preparation. Silica gels can be prepared by several methods (1,40,43). Most commonly, a sodium silicate solution is acidified to a pH value of <10–11. The gelling time varies, as shown in Figure 10. Syntheses include the bulk-set, slurry, and hydrolysis processes. The bulk-set process consists of preparing a silica hydrosol (gel) by mixing sodium silicate and a strong mineral acid, followed by mechanically breaking, washing the hydrogel particles free of electrolytes, drying, and activating. In the slurry process, sodium silicate solution and acid are mixed, either in batch or semicontinuously, to produce a gelatinous precipitate which is washed and dried, often by spray drying. These gels usually have a small particle size and the salts must be washed away before use. Gels can also be made directly from salt-free colloidal silica, which provides larger ultimate particle sizes and hence greater stability, along with low salt contents. Such gels may also have lower specific surface areas and larger pore diameters. Hydrolysis of pure silicon compounds such as ethyl silicate, silicon tetrachloride, and other volatile hydrolyzable silicic esters is another method of preparing gels. Although more expensive, this process produces dense gels of high purity and very small pore size.

The properties of a finished gel are determined by the size of the primary particles at the moment they aggregate into the gel network, called the gelation point (or gelation time). It is usually defined as the point at which aggregation in the sol forms a three-dimensional network that can support a stress elastically. The sol-to-gel transformation is not well defined because it occurs as a continuous increase in viscosity (40). The concentration of the primary particles in solution affects the physical properties of the gel, including the compactness of the gel network, the pH, salt concentration, temperature, and time during which the gel is aged while wet, and the mechanical pressure or shear forces applied to the gel before or during drying. Additionally, the physical properties are influenced by the temperature, pressure, pH, salt content, and surface tension of the liquid medium as it is being evaporated from the pores of the gel, and the temperature, time, and type of atmosphere in which the gel is heated after being dried (1). The type of catalyst used in gelation can have significant effects on the kinetics of the process and the structure of the silica gels formed (45,46). For some applications, silica gel is converted to pelletized or granular form by extruding pulverized gel with a binder or by shaping the hydrogel during drying. Silica can be gelled in

spherical form by spray-drying, or by spraying droplets into an immiscible liquid (emulsion polymerization). Freezing of a silica sol produces silica-gel particles of nonspherical shapes.

Characterization. When silica gel is used as an adsorbent, the pore structure determines the gel adsorption capacity. Pores are characterized by specific surface area, specific pore volume (total volume of pores per gram of solid), average pore diameter, pore size distribution, and the degree to which entrance to larger pores is restricted by smaller pores. These parameters are derived from measuring vapor adsorption isotherms, mercury intrusion, low angle x-ray scattering, electron microscopy, gas permeability, ion or molecule exclusion, or the volume of imbibed liquid (1).

Surfaces can be categorized as fully hydroxylated, in which the surface consists solely of silanol, $-\text{Si}-\text{O}-\text{H}$, groups, a siloxane, $-\text{Si}-\text{O}-\text{Si}-$, or an organic surface. Silanol surfaces are formed by drying silica gels or precipitates from water at temperatures below 150°C . These surfaces are readily wetted by water. Hydroxylated surfaces heated from $300-1000^{\circ}\text{C}$ progressively develop a siloxane surface by dehydration such as that found on pyrogenic silica surfaces. The behavior of particles having organic surfaces depends on the coating material. The particles may become dispersible in water, oil, or other organic solvents. If fluorocarbons are the surface group, the silica becomes both hydrophobic and oleophobic. The nature of the surface can be determined by measuring the heat of nitrogen adsorption, dye adsorption, infrared adsorption, or chemical analysis (1,28,33-37).

Modifications. Once a gel structure is formed, it can be modified in the wet state to strengthen the structure or enlarge the pore size and reduce surface area, through a process called aging (1,40,47). Silica gel reinforcement can be carried out in several ways: (1) active silica, ie, low molecular weight polysilicic acids (1), can be added to a broken-up gel in order to deposit it at a uniform rate on the gel; (2) active silica can be added to a sol as the gel is growing, causing strong gel bridges to form between particles; (3) wet gel can be heat-aged to increase coalescence of the particles.

In this aging process, silica is dissolved from smaller particles and deposited at the points of contact between larger particles. Condensation reactions in the gels continue to occur because of the presence of the silanol, $-\text{Si}-\text{O}-\text{H}$, groups (48,49). Because of the formation of new siloxane bonds that bridge the particles, the continued polymerization reactions strengthen and stiffen the network (47). Washing can also be an aging step because aging a wet gel can increase interparticle bonding, which leads to less shrinkage of the gel during drying. Low density silica gels are made by minimizing shrinkage during drying by reinforcing the gel by aging, or by replacing the water with a liquid of lower surface tension, for example an alcohol. The gel is then heated to a temperature above the critical point of the liquid, thereby releasing the liquid as a vapor. Supercritical drying is often used in aerogel processing (1).

Sintering, or heating to convert a powder into a continuous mass, a dried silica surface in air or in a vacuum causes shrinkage that decreases the surface area, whereas sintering in steam increases pore size. For example, micropores are obtained by heating a hydrated gel at 1000°C for 10 hours. The presence of impurities such as aluminum tends to minimize changes caused by heating.

At temperatures gel is converted to small pores can be adsorbents for wide pore size.

Applications

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Precipitation of Silica

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Properties

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Preparation

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At temperatures $>1000^{\circ}\text{C}$, however, and in the presence of impurities, silica gel is converted to cristobalite or nonporous silica glass. Gels having extremely small pores can be made. Such gels include impervious silica, porous glass, and adsorbents for which the applications are tailored to surface properties and pore size.

Applications. Approximately 80,000 metric tons of silica gels were manufactured in 1994 (38), primarily by Crosfield, Grace, PQ, and SCM in the United States; by CECA (France), Chemische Fabriken Oker und Braunschweig (Germany), Grace (Germany), and Solvay (Germany) in Europe; and by Dohkai, Mizusawa, and Tokai in Japan. The largest application areas for silica gels include health care products as thixotropic agents in cosmetics (qv) and dentrifices (qv); selective absorbents to maintain clarity during the brewing of beer; desiccants; thixotrope and flattening agents in coatings (50); and supports for polymerization catalysts. Specialized silica gels that have uniform pore structure, and which are often surface-treated, are used in the production of chromatography (qv) columns for gas- and liquid-phase separations. Amorphous silica gels (51) and aerogels (52) are also used as insulating materials and sol-gel coatings for optical applications (53).

Precipitated Silica

Particulate silica is composed of aggregates (or secondary particles) of ultimate (or primary) particles of colloidal-size silica that have not become linked in a massive gel network during the preparation process. Particulate silicas are either made from the vapor phase to form pyrogenic (or fumed) silicas, or by precipitation from solution, generally aqueous, to form precipitated silicas. Particulate silica powders have a more open structure with higher pore volume than do dried pulverized gels, as can be seen by comparing Figures 6 and 9 to Figure 8.

Properties. The physical and chemical properties of precipitated silicas can vary according to the manufacturing process. Ultimate particle and aggregate sizes of silicas precipitated from solution can be varied by reinforcement and control of suspension pH, temperature, and salt content value. The surface area, as determined by nitrogen (17) or CTAB (18) adsorption, is a function of the ultimate particle size, which can range from 5 to 50 nm in diameter. Aggregates are three-dimensional clusters of ultimate particles (see Fig. 9), which range in size up to approximately 500 nm in diameter. Ultimate particles in aggregates are covalently bonded to one another via siloxane bond formation. Aggregate particles can be physically agglomerated through hydrogen bonding of surface silanol groups to one another, thus affording structures that can range up to approximately 100 μm in diameter. The median agglomerate particle size is generally 20 to 50 μm in diameter, but can be reduced in size by milling, for example, to approximately 1 μm .

Preparation. Precipitated silica is formed from an alkaline metal silicate solution, such as sodium silicate in a ratio of approximately 2.5–3.3 $\text{SiO}_2:\text{Na}$. Lower concentrations of silicate are used in silica gel preparation. In the absence of a coagulant, silica is not precipitated from solution at any pH value (1). Silica is precipitated by adding acid to sodium silicate to reduce the pH value of the hot suspension to a pH value of 9–10, where the concentration of sodium

ion exceeds approximately 0.3 *N*. Sulfuric acid, hydrochloric acid, and carbon dioxide are examples of acids used commercially to neutralize sodium silicate and precipitate silica. Figure 13 shows a schematic of this process. Precipitation proceeds in three basic steps: forming colloidal particles through nucleation and particle growth to the desired ultimate particle size; coagulating colloids into aggregates to form a suspended precipitate, where the control of pH and sodium ion concentration is critical; and reinforcement of the aggregate particle to the desired degree without further nucleation (1) so that the structure is not altered.

Coagulation can also be induced by using polyvalent metal cations such as calcium ions, as well as by using ammonium and fluoride ions, and certain organic compounds. Reinforcement can be carried out by adding active silica, low molecular weight polysilicic acids, to the aggregate suspension under alkaline conditions above 60°C, or by adding acid and metal silicate at a controlled rate so that active silica forms and is polymerized on the suspended silica without forming new particles. To obtain a dry precipitate by water removal, the ultimate particles should be larger than approximately 10 nm, typically >20 nm, and the aggregates should be reinforced so that the pore structure does not collapse upon drying as a result of capillary forces. This reinforcement of the silica aggregate is characterized by the buildup ratio, which is the ratio of the final weight of silica in the system to the weight of the aggregated silica. Buildup ratios of less than 4:1 are usually preferred in order to achieve, for example, dispersibility in rubber. For each type of precipitated silica there is an optimum degree of reinforcement for maximum dispersibility (1).

Modifications. Precipitated silicas are hydrophilic and may contain up to approximately 10% water as surface silanol, $-\text{Si}-\text{O}-\text{H}$, groups that remain after drying at 150°C. The interaction of the surface of amorphous silicas with organic molecules is strongly affected by the degree of hydroxylation of the silica surface.

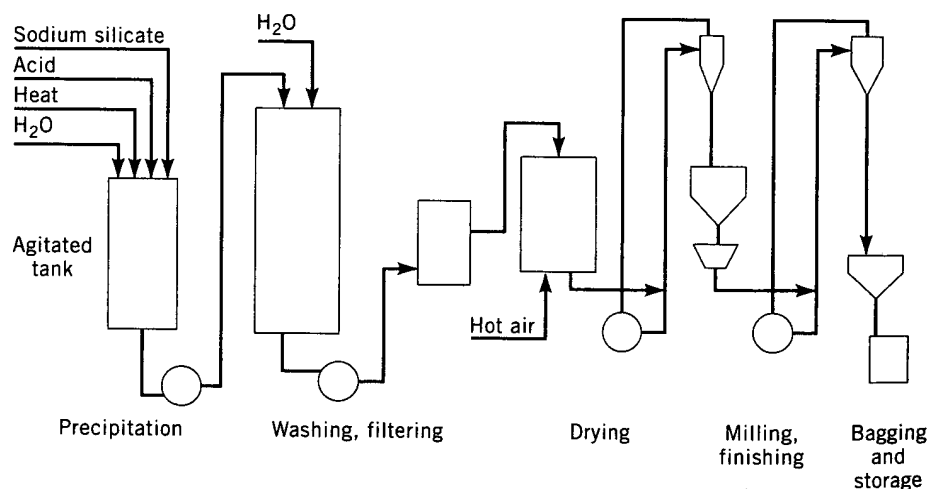


Fig. 13. Schematic of precipitated silica production (54), where \square = operational unit, eg, reactor, washer, filter, and dryer; \circ = pump or transfer device, eg, bucket elevator and air conveyor; ∇ = storage bin; \triangle = optional size modifier, eg, mill and granulator.

Thus, modification is an important step to modify the surface of polar polymers. (1) of surface modification (SUPPLEMENT). 9 coupling agents and

Application:

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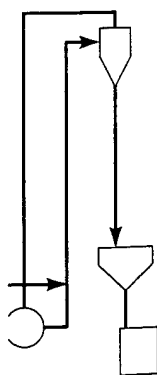
Precipitated reinforcement of directly related the ultimate particle size has resistance to pass (67-69). Newer sizes and intricate reinforcement of tire in tires.

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Thus, modification to hydrophobize the surface of a precipitated silica can be an important step toward increasing its compatibility with substrates such as non-polar polymers. The choice of appropriate modifying substance and the method of surface modification are important (see SURFACE MODIFICATION TECHNIQUES (SUPPLEMENT)). Surfactant (55–57), organosilane (58), and organotitanate (59) coupling agents and polymeric films (60,61) may be employed.

Applications. In 1994, approximately 675,000 metric tons of amorphous precipitated silica were manufactured for sale (38,62). Degussa, J. M. Huber, and PPG in the United States and in Europe, and Akzo (Germany), Alufloor (Sweden), Crosfield (United Kingdom), Nippon Silica (Japan), Rhône-Poulenc (France), Shionogi (Japan), Tokuyama Soda (Japan), and Vitro PQ (Mexico) are the primary producers.

Additionally, precipitated silica is manufactured and utilized internally for such uses as extenders for detergents and cleaners. Because of the small particle size and complex aggregate structure (see Fig. 9), precipitated silica imparts the highest degree of reinforcement to elastomer compounds, eg, natural rubber, among all of the mineral fillers (see RUBBER, NATURAL). This superior reinforcement is employed in a variety of rubber compounds for shoe soles, industrial rubber goods, and tires (63). Precipitated silica is used in shoe soles for its resistance to wear and tearing, for its nonscuffing characteristics, and in order to obtain compounds having light color, or even a transparent material. In addition, precipitated silica is used to improve the tear strength and resistance to flex fatigue, ie, cracking and cut growth, and heat-aging in a wide variety of manufactured rubber goods, including conveyor and power transmission belts, hoses, motor and dock mounts, and bumper pads. Rubber rolls that utilize the abrasion resistance, stiffness, and nonmarking characteristics of precipitated silica are important for use in paper processing and the dehulling of grains, particularly rice (see WHEAT AND OTHER CEREAL GRAINS) (64).

Precipitated silica is used in a variety of tire applications (Fig. 14). The reinforcement of rubber compounds by precipitated silica has been found to be directly related to the surface area of the silica (65,66), which is a function of the ultimate particle size. The use of precipitated silica at very high levels in tire treads has been shown to impart outstanding wet traction and rolling resistance to passenger tires, which improve vehicle handling and fuel economy (67–69). Newer grades of precipitated silica having smaller ultimate particle sizes and intricate aggregate structure (70) have shown exceptionally high reinforcement of tire tread compounds (71) and the potential for improved treadwear in tires.

Additional uses of amorphous precipitated silica include reinforcement of specialty elastomers, especially those based on polydimethylsiloxane (72); defoamer in paper processing (73) and an ingredient for good ink retention; production of polyethylene/silica membranes used as separators for plates in lead-acid batteries (qv) (74,75); control of viscosity in dentrifice (76) and coating formulations (77); abrasive ingredient in toothpaste (76) and polishing formulations; absorbent of liquids in food applications (78), animal feedstocks, and fire extinguishers; starting material for high purity zeolite manufacture; gloss control agent in coatings and plastics; carrier for active ingredients such as pesticides (79); and extender for detergents, papers, and coatings (54).

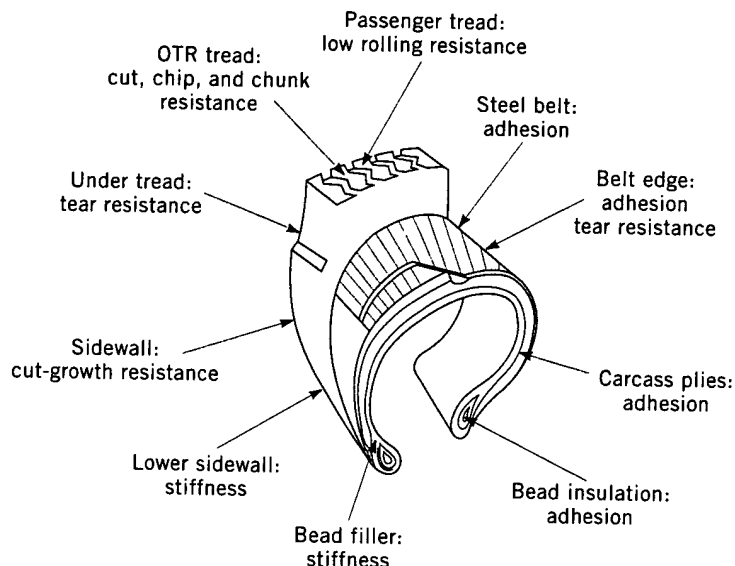


Fig. 14. Schematic of a passenger tire showing individual components and use of precipitated silica to improve rubber compound performance. OTR = off-the-road.

Pyrogenic Silica

Properties. Amorphous pyrogenic (fumed) silicas are fluffy white powders that are generally less dense and of higher purity than are silicas precipitated from solution. Pyrogenic silicas have a much lower hydrated surface and are sometimes completely anhydrous. Surface silanol density normally ranges from $2-4/\text{nm}^2$ of surface area. The particle size is controlled by combustion conditions during the flame hydrolysis. Pyrogenic silicas having surface areas $<300 \text{ m}^2/\text{g}$ are essentially nonporous, whereas those having higher surface areas can have some porosity. They generally can contain a few hundred ultimate particles fused into branched-chain, three-dimensional aggregates (54) (eg, see Fig. 6). Pyrogenic silicas in the 100 nm to 2 μm diameter particle size range are common (80).

Preparation. Pyrogenic silica can be prepared in several ways, including vaporizing silica and oxidizing organic or inorganic silicon compounds. Vaporizing silica at high temperatures of approximately 2000°C forms anhydrous amorphous silica particles upon cooling. In the presence of a reducing agent such as coke, silica sublimates at about 1500°C to produce the volatile silicon monoxide, SiO , which can then be oxidized to produce particulate fumed silica, SiO_2 . Oxidation of silicon tetrachloride, SiCl_4 , vapor at high temperatures produces fumed silica and Cl_2 . Alternatively, silicon tetrachloride can be burned in the presence of methane, CH_4 , or hydrogen, H_2 , gases to produce fumed silica, H_2O , and HCl . The latter process is an important commercial method (Fig. 15) (54). Silicon ester vapors can be oxidized and hydrolyzed to produce particulate silica of high purity, though at high cost. Silicon tetrafluoride, SiF_4 , a by-product of the phosphate fertilizer industry, can also be used to produce pyrogenic silica by hydrolysis of

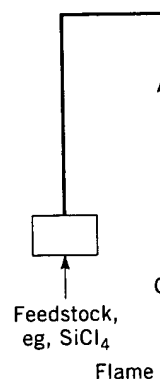


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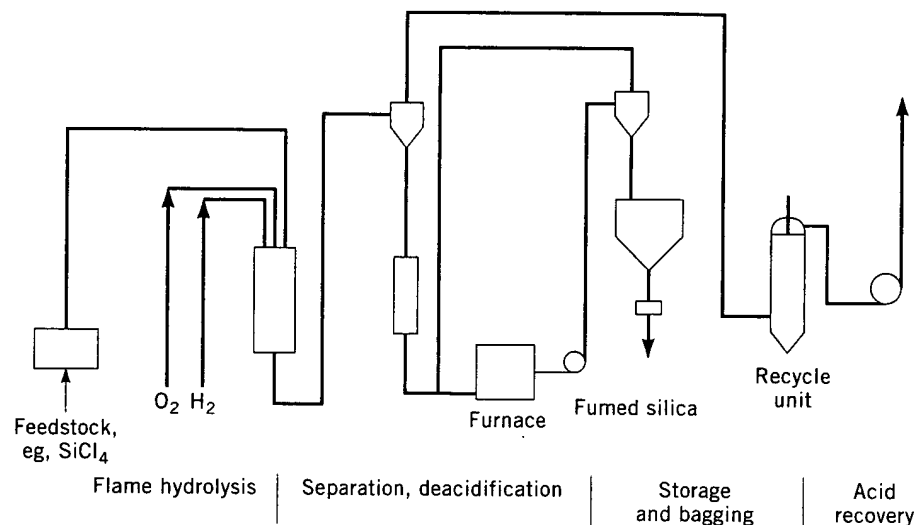


Fig. 15. Schematic of pyrogenic silica production (54). See Figure 13 for definitions.

the vapor at 1600–2200°C. HF is a by-product that can then react with sand to produce more SiF_4 (1,81).

Applications. Pyrogenic or fumed silica production in 1994 was estimated to be 140,000 metric tons (38). Cabot and Degussa in the United States and in Europe, General Electric (United States), Nippon Aerosil (Japan), and Tokuyama Soda (Japan) were the largest manufacturers. Pyrogenic silica is used in rubber applications that require a low level of surface water per unit surface area of the silica, primarily as a reinforcement in adhesives, sealants (82), and elastomer compounds based on silicone polymers (83,84). Pyrogenic silica also has a variety of other uses. It serves as a thixotropic agent in plastics, eg, in polyester casting resins; gel coats (85); sealants and adhesives (86); cosmetics in ointments and lotions (87); toothpastes; coatings (85); printing inks (88); free flow, antistatic agent in animal feedstuffs and hygroscopic powders; carrier for active ingredients such as pharmaceuticals (qv), catalysts, and liquid spice extracts (89); gloss control agent in coatings and foils (54); coating additive to improve the mechanical reliability of fused silica optical fibers (90); and antifoaming or defoaming agent in the manufacture of paper, decaffeinated coffee and tea, poultry and seafood processing, and oil refining (91).

Fused Silica

Transparent fused silica can be formed at a temperature of 1200°C and a pressure of 13.8 MPa (2000 psi) from silica powder consisting of 15 nm ultimate particles (92) or by electric arc fusion of pure silica sand having low iron and alkali metal contents. The cooled product is ground to the desired particle size. Fused silica is primarily manufactured by C-E Minerals, Minco, and Precision Electro Minerals in the United States; by Chuo Denko, Denki Kagaku Kogyo, NKK,

Showa Denko, and Toshiba Ceramics in Japan. Based on 1988 data and projected growth, an estimated 135,000 metric tons of fused silica were used in 1994 as a sacrificial component or investment casting in the manufacture of metals and as a component in refractory materials (62).

Naturally Occurring Amorphous Silica

Formation. Most naturally occurring amorphous silica deposits are biogenic forms deposited from the exoskeleton, plates, or spines of aquatic organisms such as diatoms, radiolarians, silicoflagellates, and certain sponges. These organisms extract silica from very dilute solutions, eg, 0.1 ppm of SiO_2 or 2 mmol/kg, and are found in both marine and freshwater environments. Large deposits of these materials are found as loosely coherent chalk-like sediments in the equatorial Pacific area, ie, radiolarians, and in high latitude areas of all oceans, ie, diatoms. All biogenic silicas are noncrystalline because the kinetic barrier to crystallization is high (ca 800 kJ/mol (191 kcal/mol)) in neutral aqueous environments. In all these structures the mineral exists as a hydrated, covalent inorganic polymer having the general structure $(\text{SiO}_{n/2}(\text{OH})_{4-n})_m$, where m is a large integer representing the degree of polymerization and n ranges from 0–4 to indicate the degree of hydration (93).

The silica structure has a close relationship to the cellular structure of the organism. Silica is deposited as gels, sheets, fibers, tubes, and globular assemblies. It has been found that the macroscopic geometric structure of the deposited silica is replicated in the short-order (two- to three-siloxane unit) structure (93). Although the dissolution of silica is inhibited by inclusion of various metal ions in the structure and often an organic coating, these deposits are converted over millions of years to opal-CT and opal-C, which are well-crystallized cristobalite (94). These siliceous materials are also transformed by dissolution, precipitation, recrystallization, and compaction over geological time to form a less soluble, denser material, which is called chert if granular, chalcedony if fibrous, or flint if dark gray. Amorphous silica can be formed by the alteration of sand to a colloiddally subdivided high surface area, amorphous silica volcanic ash (1). Amorphous silica is sometimes precipitated from the hot supersaturated waters of hot springs (siliceous sinter) and geysers (geyserite) where it is often found along with calcareous sinter (95,96).

Applications. The most significant commercial material from the biogenic silicas is diatomaceous earth [7631-86-9], also called kieselguhr or diatomite (qv). These deposits are the sediment of fragments and shells of one-celled algae, which form very fine particles having high surface area and as high as 94% silica content. Initially, silica in diatomite is amorphous, but portions of these deposits have been converted to cryptocrystalline quartz (95). Approximately 1,500,000 metric tons of diatomaceous earth were used in 1994 as absorbents, fillers, insulating materials, and polishing agents, primarily in China, France, Germany, Italy, Korea, Mexico, and the United States. Tripoli, a white-to-gray, soft, porous material used as an abrasive or a filler, is mined from the Devonian deposits in southern Illinois. It is sold as amorphous silica, although it is actually a microcrystalline quartz ($<10 \mu\text{m}$ dia) formed by leaching of carbonates from calcite- or dolomite-bearing chert (see ABRASIVES; FILLERS).

Health and Safety

Amorphous silica is not found in most drinking water and is not soluble in water.

Unlike crystalline silica, amorphous silica is not a cause of silicosis (97), even when inhaled. It is assumed to be a nonhazardous material. Crystalline and amorphous silica are not listed as hazardous in the 12 to 18 month period of the dust collection. In monkeys, the internal organs and the presence of silica in the monkeys were not exposed to the presence of silica.

Amorphous silica is not listed as a cause of dermatitis or respiratory irritation.

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